CHAPTER 7 THE ROLE OF TOXICOLOGY IN THE APOLLO SPACE PROGRAM

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Introduction

It had been determined from experiences with manned chamber tests and submarine operations that human exposure to trace levels of a significant number of gases presented a threat, both to man and to the successful completion of closed-loop operations. It was therefore of major concern that adequate protection be provided for space crews. This protection could be accomplished by eliminating, or at least minimizing, crew exposures to possible harmful levels of trace contaminant gases contained in the spacecraft cabin.

A review of the offgassing characteristics of nonmetallic materials used in the manufacture and fabrication of pre-Apollo spacecraft indicated that, without proper safeguards, a potential toxicological problem could develop in the Apollo spacecraft cabin. The offgassing from man and nonmetallic materials, such as surface coatings, adhesives, elastomers, cleaning agents, solvents, and spacecraft fluids systems (heat exchanger liquids, fire extinguishers, etc.), were all known to contribute to the overall spacecraft trace contaminant burden. The trace contamination problem in the spacecraft atmosphere was further complicated by the introduction of a new generation of fire retardant materials following the Apollo 204 fire. Most of these materials were of the halogenated polymeric type and had undergone few or no toxicity investigations.

Toxicological Considerations

When toxicology is discussed, lethality is generally the major concern. It was equally important, however, in the Apollo Program, to ensure that a crew's exposure to a contaminated atmosphere created no irreversible physiological changes. Irreversible decrements in any physiological function were considered completely unacceptable. Had this criterion not been met, the ability of the crew to properly perform their duties throughout the mission could have been seriously hampered and the success of the mission jeopardized.

Most of the available inhalation toxicity information concerning man is based on the eight-hour work period of the industrial worker. Such data presumes an eight-hour daily

exposure, followed by a 16-hour recovery period prior to re-exposure, and a 48-hour weekend recovery. New exposure limits had to be established for space missions since these involved uninterrupted exposure for two weeks with no daily or weekend recovery periods. Information concerning the possible resultant cumulative damage was unavailable.

Two major toxicological situations were considered to develop a toxicology program that could best be used to evaluate the factors involved in extended human exposures. These were the potential contaminant levels that could occur during (1) "normal" spacecraft operating conditions, that is all spacecraft systems functioning properly, and (2) the "emergency" situation, that is when any spacecraft system experienced an upset condition or a failure mode. In the normal condition, the major concern was generation of trace contaminant gases by the normal offgassing of nonmetallic materials both at ambient temperatures and at elevated temperatures during equipment operation. Other sources of contaminant gases under normal conditions were the breathing gas supply reservoirs onboard the spacecraft and, to a lesser extent, the crewmembers themselves. Under emergency conditions, contaminant gas levels could be quantitatively much greater because of overheating, spills, ruptures, and so forth. Rupture of the coolant loop, for example, could have introduced a dangerous contaminant, ethylene glycol. Pyrolysis of some of the electronic nonmetallic materials could have produced a host of particulates and toxic gases.

Provisions were made in the spacecraft carbon dioxide removal unit for the removal of trace levels of contaminant gases. The unit consisted of two parallel canisters, each containing lithium hydroxide for removal of carbon dioxide, and activated carbon for the removal of trace contaminant gases. The parallel flow configuration permitted the canisters to be alternately exchanged for fresh ones after 12 hours of continuous operation. While activated carbon is the best all-purpose trace contaminant gas removal agent, it does not remove carbon monoxide. The only means for removing carbon monoxide from the spacecraft cabin was by cabin leakage. Since leakage rates were very low, the presence of carbon monoxide in the spacecraft cabin was a major concern for all the Apollo missions.

In summary, two major areas of emphasis in the toxicology program were (1) sources of contaminant gases and (2) control or removal of these gases. The trace gas source problem was dealt with by implementing a spacecraft materials control program to either eliminate or minimize the acceptance of materials with undesirable offgassing properties. A trace gas removal capability was incorporated in the spacecraft environmental control system to maintain an acceptable trace gas level in the spacecraft cabin. Before either of these programs could be intelligently implemented, however, maximum acceptable concentrations had to be determined for trace contaminant gases in the spacecraft cabin.

Maximum Allowable Concentrations of Spacecraft Trace Gas

A major difficulty existed in deriving a set of maximum allowable concentrations (MAC) for spacecraft trace contaminant gases. "New" toxicity values had to be determined with a dearth of data concerning increased exposure time and human responses to different compounds or mixtures of compounds.

Thomas (1968)* characterized human toxicity responses in a generalized manner, in the following ways:

- 1. Equilibrium (intake equals excretion). The total organism appears to maintain equilibrium, since the excretion of the contaminant equals the intake or input. There is no apparent biochemical reaction.
- 2. Adaptation (desensitization, cross tolerance). There may be chemical reactions, but these are countered by an adaptation of the organism to the contaminant exposure.
- 3. Cumulative (summation of interests). The adsorbed contaminant damages one or more internal organs, with concomitant biochemical derangement and probable physiological dysfunction.
- 4. "All or None" (carcinogens, sensitizers, irritants). Response may be immediate, as with irritant substances, or delayed, as with sensitizing substances. Some materials may be involved in cancer production. (Carcinogenic reactions were not considered in the Apollo toxicity program.)

Considering these generalized response descriptions in relation to the differences in the maximum allowable concentration values for the eight-hour work day exposure versus the approximately 350 hours of lunar space mission exposure, it is noteworthy that, in most cases, one or all four types of these responses were significant in determining new MAC values for the lunar mission. In the cases for the "equilibrium," "adaptation," and "all or none" responses, the alterations of the MAC values could be theoretically small or none at all. In the case of the "cumulative" response, the MAC value required a major reduction since the change in exposure duration was increased by a factor of approximately 44 times the original exposure time value. It was realized that it was virtually impossible to consider the synergistic effects of two or more compounds in establishing the spacecraft MAC levels.

Establishment of Spacecraft Materials Selection Criteria

During the initial phases of the Apollo Program, a procedure was adopted that served as a toxicological screening test for spacecraft candidate nonmetallic materials. This test was used to determine the toxic effects of the offgassed products on laboratory animals. The test consisted of heating materials to 341°K (68°C) and allowing the offgassed products to flow over rats and mice for a period of 14 days. Weight losses of each material were recorded, and the exposed animals were observed for their responses. The animals were observed periodically for 30 days after exposure, and histopathological studies were made.

In all, 150 materials were tested at the Wright-Patterson Air Force Base Toxicology Facility. Approximately 10 percent of the materials tested were rejected because they produced unsatisfactory responses in animals. Approximately 90 percent of the materials tested offgassed significant amounts of carbon monoxide.

^{*}A.A. Thomas: Man's Tolerance to Trace Contaminants. AMRL-TR-67-146, Aerospace Medical Research Laboratories, Wright-Patterson Air Force Base, Ohio, Jan. 1968.

With the change of materials specification after the Apollo 204 fire, only about 20 percent of the information previously obtained was applicable for the fabrication of subsequent spacecraft. The revised materials program emphasized the requirement for low flammability characteristics. At that phase in the program, there was insufficient time to conduct toxicological studies on the newly developed materials as had been done earlier. A new screening test was adopted that included offgassing considerations so that appropriate information would be available for the selection of the candidate materials. As before, the candidate material was heated to 341°K (68°C) but animal exposures were replaced with analytical analyses. The material was kept at 341°K (68°C) for 72 hours in a dessicator filled with oxygen to a pressure of 337 x 10²N/m² (253 mm Hg). At the end of the 72-hour period, samples of the dessicator atmosphere were withdrawn for determination of the amounts of total organics (TO) and carbon monoxide (CO). Results were reported as micrograms of TO or CO per gram of material offgassed. Any material tested was considered acceptable if it offgassed less than 100µg TO or 10µg CO per gram of material.

An odor test was also employed to test for those materials considered undesirable because they generated offensive odors. This test was accomplished by allowing a specially qualified panel of laboratory personnel to grade their odor responses to an administered sample of the atmosphere from the candidate material.

In cases where it was known that a candidate material might undergo overheating in the actual spacecraft application, pyrolysis studies were employed using laboratory animal exposures and analytical chemistry. The final decision, from a toxicological standpoint, was then made for the data obtained.

Materials Acceptance

One of the main functions of the Johnson Space Center Toxicology Laboratory was to provide a rapid response capability for handling emergency toxicity problems. Most often the emergency problems resulted in one of three resolutions. A material usage or procedure was either (1) approved, (2) disapproved, or (3) approved after modification.

During the Apollo Program some thirty of these emergency problems were resolved. Some examples are listed below:

Disapproved. Carboxynitroso rubber was submitted as a candidate material for use as an electrical insulator. Upon pyrolysis, the material was found to produce a very toxic vapor. A flight log ink was found to produce toxic volite vapors at room temperature.

Approved. Ethylene glycol was selected as the candidate heat exchanger fluid for the Command/Service Module. It was feared that even a minute leak in the spacecraft coolant loop could result in a hazardous breathing atmosphere. A series of contractual and in-house studies proved the problem could be handled by training the astronauts to detect trace levels of the glycol vapor. Several paints and adhesives were found to offgas excess quantities of total organics. These materials were all approved for usage after a qualitative analysis proved the offgassed species to be nontoxic at the levels offgassed.

Approved After Modification. A special paint developed for the space program was found to offgas excessive quantities of total organics and carbon monoxide. The paint

was approved for usage by employing a procedural change in the curing process. A quartz window was installed in the Command/Service Module for conducting special ultraviolet photographic work. The quartz window permitted the production of ozone in the cabin atmosphere when the spacecraft orientation allowed sunlight to pass into the interior of the vehicle. The use of the quartz window was allowed by requiring the use of an ultraviolet filter over the window when photographic work was being done.

In general, the time required to conduct these special toxicity assessments was from two to six weeks. The investigation on the use of ethylene glycol was the major exception. Approximately 18 months were required for the ethylene glycol evaluation.

Atmospheric Assessment

Preflight Assessment

Prior to the first Earth orbital flights of the Apollo spacecraft, a series of solar simulator—altitude chamber tests was accomplished to determine the overall performance characteristics of the spacecraft systems. This included testing of the prototypes of the Command/Service Module (designated as 2TV-1) and the Lunar Module (designated LTA-8). These tests were conducted at the Johnson Space Center's High Altitude Chamber Test Facility. During the testing of both vehicles, trace contaminant analyses were performed on the crew cabin atmospheres to ensure the safety of the test crew and to assess the performance of the spacecraft's environmental control system in maintaining an acceptable breathing gas environment.

The atmospheric samples were taken both by whole gas sampling and by cryogenic trapping techniques. Chemical analyses were accomplished by employing the latest methods in gas chromatography, mass spectrometry, and infrared spectrophotometry.

The final atmospheric assessment of the flight Command and Lunar Modules was accomplished at the Kennedy Space Center during final checkout of the spacecraft. Atmospheric samples were taken from both vehicles prior to their acceptance for space flight. Sampling and analytical methods similar to those described previously were employed at the Kennedy Space Center for assuring the atmospheric quality of these spacecraft.

Postflight Analyses

Inflight cabin trace gas composition was determined by chemical analysis of the activated carbon canisters returned from the Apollo 7 through 17 spacecraft. The carbon dioxide concentration calculated from conversion of lithium hydroxide in the canisters was utilized to study crew metabolic performance.

Samples of activated carbon were removed from each of the canisters for trace gas analysis. The trace gas samples were obtained by employing high vacuum and thermal desorption techniques. Both qualitative and relative quantitative chemical data were obtained by performing gas chromatographic—mass spectrometric analyses on the activated carbon desorbate. A list of the identified compounds from Apollo 7 through 17 is presented in table 1. (An "X" under the mission number indicates that the compound listed was present in the desorbate taken from that mission.)

Table 1
Apollo Spacecraft Contaminants

Contaminant Name	· L	Flights in Which Detected											
	7	8	9	10	11	12	13	14	15	16	17		
Amyl Alcohol													
Butyl Alcohol	×	×	×	×	×	×	×	×	×	×			
Capryl Alcohol					×	×	×	×	×				
Ethyl Alcohol	l x	×	×	×	×	×	×	×	×	×	×		
Isoamyl Alcohol	1				×	×	×	×	×	×			
Isobutyl Alcohol	×	×	×	×	×	×	×	×	×	×	×		
Isopropyl Alcohol	×	×	×	×	×	×	×	×	×	×	l x		
Methyl Alcohol	×	×	×	×	×	×	×	×	×	×	×		
Propyl Alcohol	×				×	×	ł		×	×	×		
Sec-Butyl Alcohol	×	×	×	×	1		×						
Tert-Butyl Alcohol	l x	×	×			×							
Acetaldehyde	l ×	×	×	×	×	×	×	×	×	×	×		
Butyraldehyde	×		1		l	1			1		1		
N-Butane			1		×	×	×	×	×	×	×		
Cyclohexane	l x	×	×	l x	×	×				×	l x		
Cyclopentane	l ×		l x		×	×		×	×	l x			
Ethane			ĺ	1	×	×	×	ŀ	l ×	×	×		
Heptane	l x	×	l x	×		l x				Ì			
Hexane	×	×	×	×	l x	×	l x	i	l x	×			
Isobutane	"	'			×	×	1		×	l x			
Isopentane	l ×	×	×	×	l ~	"	ļ.		"	^	l _×		
Methylcyclohexane	^	x	x	x	×	l x	l x	×	×	×	^		
Methylcyclopentane	^	^	l â	l â	^	l â	l â	^	l â	l x	l _×		
N-Octane	^	1	^	 ^		^	^	^	^	^	1^		
Pentane	l â	×	l x	×	×	×	1	1					
Propane	1 ^	^	l ^	^	×	^			×	×	×		
Trimethylbutane	×			×	^	^			^	^	1^		
Trimethylhexane	l â		×	^			1		1	١.,			
Allene	^	l	^	l	×		×	-	1	×			
	1	١		١	l	X	X	l	1	1			
Benzene	×	×	×	×	×	X	X	×	×	×	×		
1, 3,-Butadiene		ŀ	1	1		×	X	1	l		1		
1-Butene				ì	X	X	×	×	X	X	l ×		
2-Butene (cis)	1	1		ł	х	X)		×	×	×		
2-Butene (trans)			1		x	×	•		×	×	×		
Cyclohexane		×	ł			X	×	1	x	×	ı		
Cyclopentene		×		×			1						
Ethylbenzene	1	×	×	×	×	×	×	X	×	×	×		
Ethylene	×	×		х	X	x	x	×	×	×	×		
2-Hexene	1		×	×	×	×	×	×	×	x	×		
Indene	×	×		1	X	×	×	×	×	×	×		
Isoprene			1	×	×	×	×	×	×	×	×		
Mesitylene	×		×		×	×	×	×	×	×	×		
Methylacetylene	-				x	X	×		×	×			
1-Pentene	×		×	×	1		1		×	1	1		
2-Pentene				ı	1	×	×		×	×	1		

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Table 1 (Continued) Apollo Spacecraft Contaminants

Contaminant Name	Flights in Which Detected										
	7	8	9	10	11	12	13	14	15	16	17
Dichloroethane					×				×	×	х
Dichloroethylene		l			×	×					
Dichlorofluoromethane		1			×	×	1]		
Difluoroethylene			1				×		×		×
Ethyl chloride					×	×				×	×
Ethylene dichloride	×							ĺ			
Ethylfluoride						×	×	×	×	×	×
Fluoroethane					×		×		×	×	
Fluoropropane						×	×		×	×	
Freen 11	×	X	×	x	×		×		×	×	1
Freon 12 Freon 22					×	X	×	х		×	×
Freon 113					X	х	×	х		×	
Freon 114	х	×	×	x	x	×		X	×	×	×
Methylchloride					×			1			
Methylchloroform	×	1	l			X	×		×	×	×
Methylene chloride	×	×	×	X	×	Х					×
Mono-Chloroacetylene	^	^	*	х	×	×		×	×	×	×
Pentafluoroethane		ļ			×		١		1		
Tetrachloroethane		×		١.,	×	X	×	l	x	x	×
Tetrachloroethylene	×	x	×	×		X		x			
Tetrafluoroethylene	^	^	^	^	×	×	١.,]		X	×
Trichloroethylene	x	×	×	×	l â	l ^	×		X	X	×
Trifluorochloroethylene	^	l x	^	^	^	^		x x	X	X	×
Tetrahydrofuran		^						^	×	×	
Methylfuran			ŀ						^	^	
Freon 21							1		×	×	
Hexafluoroethane		ł					1		^	l â	
Trifluoroethylene					×	×	×	x	×	×	×
Trifluoromethane					×	l ^	^	l î	l â	l â	^
Trifluoropropane						x	×	 ^	x	l x	
Trifiuoropropene					×	"	×	l I x	×	^	
Vinyl Chloride						×	×	l x	x	×	×
Vinylidene Chloride				×	×	×	×	"	x	×	×
Dimethyldiflurosilane					·	×	×	l x	~	×	^
Trimethylfluorosilane					×	l x	×	x	x	×	×
Diethyldisulfide					×					"	^
Dimethyldisulfide				×					×	×	
Dimethylsulfide			×	×	×	×		×	×	×	×
Vinyl Fluoride							×	x	×	×	×
1, 1, 1-Trichloroethane							x	x	x	×	x
Tetrafluorochloroethane							x			1	
Chlorodifluoroethylene							×	x	x		
Naphthalene							х		x		
Pentyl alcohol							х	× ,	.		
Cellosoive acetate							х .		3.29		
Decahydronapthaniene		İ					×	×			

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Table 1 (Continued)
Apollo Spacecraft Contaminants

Contaminant Name	Flights in Which Detected											
	7	8	9	10	11	12	13	14	15	16	17	
Propylene	x	×	х	х	х	×	х	х	×	×	×	
Styrene	×	×	×	×	×	×	×	×	×	1		
Toluene	х	×	×	×	×	×	×	×	×	×	×	
Trimethyl Benzene		1			×				×			
M-Xylene	х	×	×	×	×	×	×	×	×	×	x	
O-Xylene	×	×	×	×	×	×	×	×	×	×		
P-Xylene	×	×	!	i .	ĺ	×	×	×	×	×		
N-Propyl Benzene		[ŀ				ŀ		×	×		
Ethylacetylene				į .					×			
Trimethylbenzene									×			
2-Methyl Pentane							ŀ			×	×	
Dimethyl Butane				Į .		ľ			1	×	×	
3 Methylpentane											×	
Acetylene			ŀ	[×	×	×		×	×	×	
Octyne		İ		Ì		×	×	×	×			
Diisopropylamine				×								
Butyl Acetate	х	×	×	×	×				×			
Butyl Lactate			İ			×		×				
Ethyl Acetate	×	×	×	×	×	×			×	×		
Ethyl Lactate					ŀ	×	×	×				
Methyl Acetate	x	×	×	×	×	×	×		1			
Propyl Acetate	×						×		l			
Dimethyl Ether	ł		l		×	×			×	×	×	
Dioxane			×	×	×	×	×	l	×	×	×	
Furan		×	×	×	×	×	×	х	×	×	×	
Sulfur Dioxide				×							×	
Acetone	×	×	×	×	×	×	×	×	×	×	×	
Cyclohexane	×						1	1				
Methyl lethyl Ketone	x	×	×	×	×	×	×	×	×	×	×	
Methyl Isobutyl Ketone	x	×	×	×	×	×	×	×	×	×	×	
2-Pentanone	x	×				Į			İ		ļ	
Acetonitrile			×	×	×	×		×	×	×		
Methoxy Acetic acid				×		Ì		×				
Carbon Tetrachloride	×		İ					×				
Chloroacetylene			l			×						
Chlorobenzene		x	х	×	x	×		×	×			
Chlorofluoroethylene	1					×		×	×	х	×	
Chloroform	×	×			х	×	İ			x	×	
Chloropropane	×							1			1	
Chlorotetrafluoroethane					×	×		1	×		×	
Chlorotrifluoroethylene					х	×			×	×	×	
Dichlorobenzene		×	×	×		×					×	
Dichlorodifluoroethylene						×	1	×	l x	×	l x	

Table 1 (Continued)
Apollo Spacecraft Contaminants

Contaminant Name	Flights in Which Detected											
	7	8	9	10	11	12	13	14	15	16	17	
Chlorotrifluoromethane								х				
Fluoroform]		×	1			
Trifluoroacetonitride						l		1	l x			
Octalfluorobutane						l		l x				
Propadiene						1		×				
Dichlorodifluoroethane						l		×		l x	l x	
Dimethylcyclohexane						l		×	1	l x		
Cyclohexyl alcohol						l		l	×			
1-Hexene						l			l x	l x	l x	
Octafluoropropane							ľ	i	l x			
Ethyl fluoride						l			×			
Hexafluoropropene	i			İ			}		×			
Vinylidenefluoride							1		×			

Quantitative information is not included in this chapter because of the uncertainties associated with the adsorption-desorption efficiencies of the compounds listed.

Summary

This chapter has presented some of the major considerations that governed the formation and application of the toxicology program employed in support of the Apollo Program. The overriding concern of the program was the safety of crews exposed to trace contaminant gases for extended periods of time. The materials screening program employed, in conjunction with a well designed spacecraft environmental control system, helped to attain the goals set forth for the Apollo Program.

The knowledge gained from working with the toxicity problems and the identification of compounds in the space cabin atmosphere are of much importance for continued efforts in the realm of manned space flight.